Biomass Fuel Quality Enhancement and Respiratory Quotient (RQ) for Ranking Fossil and Biomass Fuels Based on CO_2 Emissions

Siva Sankar Thanapal, Dustin Eseltine, Kalyan Annamalai and Devesh Ranjan

Abstract Torrefaction is one of the thermo-chemical pretreatment techniques used to enhance the properties of biomass fuels. An inert environment is maintained during torrefaction process. Effect of using carbon dioxide (CO_2) as torrefaction medium for mesquite and juniper woody biomass was investigated in the current study. CO_2 torrefaction resulted in improved grindability and comparable energy retention in the case of mesquite and juniper. A three component model based on independent parallel reactions was developed to model the torrefaction process. Effect of torrefaction on behavior of the three components in the biomass: hemicellulose, cellulose and lignin was studied. Kinetic parameters for the three biomass components were obtained from literature. Results from the TCM were compared with the results obtained from TGA experiments carried out on mesquite and juniper samples. Further, concept of respiratory quotient (RQ) used in biological literature was applied to combustion applications. Global warming potential (GWP) of different fuels were estimated based on respective RQ. Higher the RQ of fuel, higher is its GWP. A term $RQ_{\text{PROCESS,BIOMASS}}$ was introduced to estimate the amount of CO_2 produced during processing a renewable fuel for combustion applications.

Keywords Torrefaction · Lignocellulosic biomass · Pyrolysis · Carbon dioxide emissions · Respiratory quotient · Thermo gravimetric analysis (TGA)

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1 Introduction

Coal accounts for 45 % of the total generated electricity in the United States (EIA 2013). Along with CO_2, harmful pollutants such as nitrogen oxides (NO_X), sulfur oxides (SO_X), and mercury are also released during the combustion of coal in power generating facilities. Usage of alternate renewable energy sources is investigated to reduce the impact of fossil fuels on the environment. Biofuels are one of the renewable energy sources which contribute about 10 % of the total energy in the world (EIA 2013). Desired characteristics of biomass crops which can be used for power generation were listed by Mckendry (2002). They include high yield, low energy input for production, low cost, low contaminants, and low nutrient requirements. Though wood was the dominant source of energy in the United States till 1850, its usage slowly decreased with the utilization of coal (Tillman et al. 2012). With current regulations on the emissions, the focus has again shifted toward the use of wood and other biomass fuels along with coal. The carbon dioxide emitted during the combustion of biomass fuels is supposed to be absorbed by the growing plants in the carbon cycle, and hence, biomass is considered to be carbon neutral. The term biomass includes wood, forest wood residues, agricultural wastes, energy crops, animal wastes, and municipal solid wastes.

Although biomass has been extensively studied as a renewable energy source, most research conducted used raw untreated biomass. While the use of raw biomass as a renewable energy source has potential, pretreatment of raw biomass could further enhance its capabilities as a fuel. Raw biomasses have relatively low energy contents and generally contain high amounts of moisture resulting in reduced conversion efficiency. The higher amount of oxygen contained within biomass also results in a lower calorific value. The torrefaction process directly affects the oxygen content via the liberation of volatiles that contain oxygen. This causes a decrease in the O/C ratio and results in a biomass with a larger higher heating value (HHV).

Torrefaction is a pretreatment process that aims to improve the quality of biomass by reducing the moisture content and increasing its calorific value via decreasing the oxygen percentage within the biomass. This is done by heating biomass at a constant temperature between 200 and 300 °C for a set period of time in an inert environment. Different gases which are used to maintain an inert environment includes nitrogen (Bridgeman et al. 2008; Arias et al. 2008; Almeida et al. 2010), argon (Prins et al. 2006b) and recently wet torrefaction using hot compressed water were studied to improve the energy density of biomass (Yan et al. 2010). Effect of using a small amount of oxygen on torrefaction was studied by Rousset et al. (2012) and Wang et al. (2012a). Effect of using CO_2 as the pretreatment medium was studied by Eseltine et al. (2013). Under certain torrefaction conditions, the resulting biomass can have properties comparable to low-rank coals (Chen and Kuo 2010a). Increasing the calorific content of biomass by lowering the oxygen–carbon ratio makes it more suitable for use as a fuel for gasification (Prins et al. 2006a). This coupled with the increased grindability makes torrefied biomass an attractive fuel for co-firing applications as well.

Hemicellulose, cellulose, and lignin are the main constituents that comprise the cell structure of lignocellulosic biomass. Changes in the percent of each constituent cause variation in the results obtained from the torrefaction of different biomasses. Recently, there has been a significant amount of research done on how the composition of lignocellulosic biomass influences the thermal degradation. Chen and Kuo (2010a, b) and Chen et al. (2011) have completed studies on the effect of torrefaction temperature on the lignocellulosic structure of several different biomasses. The effect torrefaction has upon the three main constituents is of particular interest due to the chemical makeup of hemicellulose, cellulose, and lignin. Understanding the chemical behavior of these components is integral in optimizing the torrefaction process. Demirbaş (2005) investigated the percent of each of the three main constituents of lignocellulosic biomass and their contribution to the HHV of the fuel. From the analysis of the structural composition, it was determined that, in general, an increase in the amount of lignin in a lignocellulosic biomass results in an increase in HHV. Elemental composition analysis of the lignin portion of each biomass indicated that lignin has an increased carbon content and decreased oxygen content when compared to hemicellulose and cellulose. This decrease in the O/C ratio between lignin and the other two constituents (hemicellulose and cellulose) is what causes lignin to have a higher HHV. Based upon the data obtained, it was determined that there is no direct relation between the hemicellulose and cellulose content of a biomass and its HHV. However, there is a good relation between the amount of lignin within a biomass and the HHV of the biomass. The importance of lignin becomes magnified in torrefied biomass due to most research (Arias et al. 2007; Chen and Kuo 2010a; Prins et al. 2006b), suggesting a mild torrefaction process (240–250 °C) for the pretreatment of biomass. Mild torrefaction, which causes a significant breakdown in hemicellulose, a moderate breakdown in cellulose, leaves lignin as the main contributor to the HHV of the resulting biomass.

The thermal breakdown of the lignocellulosic components of biomass was further studied by Wu et al. (2009) using a TGA. Three different compounds were used to model the three major components of biomass: xylan (a major component of hemicellulose), avicel (cellulose), and alkali lignin. Ultimate analysis of the three substances showed similar results compared to other literature (Demirbaş 2005), with lignin having a lower oxygen–carbon ratio than cellulose and hemicellulose. Weight trace curves and DTG analysis of the data clearly showed the thermal breakdown of each component. The majority of hemicellulose breakdown occurred between 210 and 320 °C with minimal weight loss occurring beyond 320 °C. Cellulose weight loss occurred predominantly between 310 and 390 °C with almost no weight loss occurring outside that temperature range. Lignin showed the widest range of thermal degradation with weight loss occurring between 200 and 550 °C. Related research done by Yang et al. (2007) on the pyrolytic behavior of hemicellulose, cellulose, and lignin had similar results, with the exception of lignin continuing to breakdown up to 900 °C. Since torrefaction occurs within the temperature range of 200–300 °C, thermal degradation of hemicellulose, cellulose, and lignin will occur during torrefaction, as previously shown (Chen and Kuo 2010b).

Most research on torrefaction of various biomasses has resulted in the same conclusions. Mild torrefaction temperatures (240–250 °C) produce biomass that is hydrophobic in nature (Arias et al. 2007), while the resulting heating value yield remains relatively high. Residence temperature has been shown to have a much greater effect upon the chemical changes than residence time. Previous work (Arias et al. 2007) has indicated that residence times beyond 1 h have no significant impact upon the fuel properties of biomass. The weight loss that occurs from mild torrefaction is highly dependent upon the hemicellulose fraction of the biomass being torrefied due to the thermal degradation of hemicellulose occurring below 280 °C. Limited studies were done on the torrefaction capability of CO_2. Considering the temperature limits for Boudouard reaction, the effect of using CO_2 under the pretreatment conditions (200–300 °C) should be studied further (Thanapal et al. 2014).

Thermogravimetric studies have been done to extract the kinetic constants: activation energy and pre-exponential factor from the biomass pyrolysis data. A number of studies have focused on determining the effect of heating rate on pyrolysis of biomass (Biagini et al. 2006; Vamvuka et al. 2003). Different methods have been used to determine the kinetic constants to predict the release of volatile matter from biomass. Some of the common methods which are used to determine the reaction kinetics includes Broido–Shafizadeh model for the pyrolysis of cellulose (Bradbury et al. 1979), Ozawa (Ozawa 1965), single reaction conventional Arrhenius (Chen 2012), independent parallel reactions (Hu et al. 2007; Wang et al. 2012b; Mészáros et al. 2004; Manya et al. 2003), successive reactions (Varhegyi et al. 1989), and distributed activation energy method (Anthony et al. 1976; Sonobe and Worasuwannarak 2008). The kinetic parameters have been determined for individual components of biomass materials: hemicellulose (Peng and Wu 2010), cellulose (Antal and Varhegyi 1995), lignin (Faix et al. 1988; Ferdous et al. 2002), and extractives using the above-mentioned methods. A comprehensive review by Di Blasi (2008) gives detailed information on studies done on the pyrolysis of biomass including different models for pyrolysis process.

Kinetics of pyrolysis of biomass and other fuels are useful for modeling the combustion reactions occurring within a burner. Also such kinetics can be used to determine the amount of mass loss which occurs during thermal pretreatment processes such as torrefaction. Limited studies have focused on utilizing the kinetics extracted from the pyrolysis of biomass constituents on the modeling of torrefaction. Prins et al. (2006c) used a two-step reaction mechanism to model the torrefaction of willow in the temperature range of 200–300 °C. Repellin et al. (2010) used three models to predict the mass loss during the torrefaction process. A simple model based on global weight loss kinetics, Di-blazi Lanzetta two-step reaction model, and Rousset model to study the torrefaction process.

In addition to reduced transportation costs, the improved quality results in lower CO_2 emission per unit amount of energy released. While biomass is considered as a renewable fuel and as such CO_2 emitted during combustion is not considered as emission, the production of such biomass fuel (e.g., ethanol) still involves use of fossil energy which releases CO_2. Thus, it is of interest to formulate a rating system for all fuels including renewable biomass fuels which will directly yield CO_2 emitted in tons per GJ of energy release. Biology literature defines RQ as a ratio of moles of CO_2 produced (or CO_2 eliminated) to stoichiometric oxygen (O_2) moles consumed typically during oxidation reaction, e.g., oxidation of nutrients in the body which results in release of energy for maintaining the normal warmth (37 °C) of the body. The RQ factor for fat, protein, and carbohydrates, the three basic nutrients of the body, is 0.7, 0.8, and 1, respectively (Hall 1905; Richardson 1929; Morinaka et al. 2012; McClave et al. 2003). However, senior citizens have problem of excreting $CO_{2,}$ and hence, they are prescribed low RQ diet (e.g., fat with low RQ). Such a concept has been recently introduced in thermal systems in order to select low RQ fuel for power generation (Annamalai 2013). This method of RQ concept for estimating the CO_2 emission from different fuels was elaborated here to estimate the global warming potential (GWP) of fossil and as well as renewable fuels.

Current chapter presents the results obtained from TGA studies on CO_2 torrefaction of woody biomass which dominates the rangelands and grasslands of southwestern United States (mesquite and juniper), batch torrefaction of samples using a laboratory oven, modeling the weight loss during torrefaction using a three-component model and application of RQ concept to estimate GWP of different fuels.

2 Materials and Methods

2.1 Thermogravimetric Analyzer

All TGA tests were performed utilizing a TA Instruments Q600 thermal analyzer located at the Coal and Biomass Energy Laboratory (CABEL) at Texas A&M University. Ground biomass samples of size between 540 and 890 μm were used for the TGA tests. Around 10 mg sample was used for each TGA study. The instrument is capable of highly reproducible measurements with ±1 % accuracy. The purge gas flow was regulated to below 20 psi using a pressure regulating valve attached to the purge gas tank. During experiments, the flow rate of the purge gas was controlled via the TA Instrument Explorer software installed on the connected PC and regulated via the internal mass flow controller in the Q600. Purge air was used after each test run to cool the furnace back to an ambient temperature. The TA Instrument Explorer software allows for direct control of several test parameters and can also be utilized to create a step by step test procedure. Two separate test procedures were used for the torrefaction and pyrolysis tests completed with the Q600. A constant heating rate of 20 °C/min was used for the pyrolysis tests where the samples were heated from room temperature till 900 °C. For the torrefaction tests, the samples were heated at a constant heat rate till the torrefaction temperature and then maintained at the same temperature for a given time period. After the torrefaction process, the samples were again heated at a constant heating rate till 900 °C. All the tests were carried out in an inert environment by flowing nitrogen, argon, and carbon dioxide depending upon the environment which has to be used for the torrefaction and pyrolysis study.

2.2 Laboratory Oven and Grindability Tests

In order to obtain higher amount of samples for determining the fuel properties and study grindability, 5 g of samples were torrefied in a laboratory oven. The samples were prepared by heating at a constant rate of 20 °C/min from room temperature till the optimum torrefaction temperature. The samples were then torrefied at the given torrefaction temperature for a constant time period. Three torrefaction mediums were used for preparing the samples: nitrogen, carbon dioxide, and argon.

Both raw and torrefied samples were shipped to a third party commercial evaluation laboratory for fuel property analysis. After large-scale torrefaction using the laboratory oven, torrefied and raw biomass samples were tested for grindability. The grindability tests consisted of sieve analysis (size distribution analysis) and sample grinding using a Sweco model DM1 grinding mill. All samples were ground for 20 min so that the amount of energy used in grinding the samples was held constant.

2.3 Torrefaction Model

For a biomass material composed of hemicellulose, cellulose, and lignin represented in a carbon-normalized form, mole balance can be represented as

$$\mathrm{CH}_m\mathrm{O}_n \rightarrow n_{\mathrm{hemi}} \times \mathrm{CH}_{\mathrm{hh}}\mathrm{O}_{\mathrm{oh}} + n_{\mathrm{cell}} \times \mathrm{CH}_{\mathrm{hcell}}\mathrm{O}_{\mathrm{ocell}} + \mathrm{n}_{\mathrm{lig}} \times \mathrm{CH}_{\mathrm{hl}}\mathrm{O}_{\mathrm{ol}}$$

where m and n stand for the number of hydrogen and oxygen atoms, respectively, in the carbon-normalized fuel. From the atom balance; known percentage composition of hemicellulose, cellulose, and lignin; and H/C and O/C ratios for hemicellulose and cellulose, one can determine H/C and O/C for lignin. The heating value of the biomass can be represented in terms of the composition of the individual components.

$$\mathrm{HV}_{\mathrm{biomass}} = Y_{\mathrm{hemi}} \times \mathrm{HV}_{\mathrm{hemi}} + Y_{\mathrm{cell}} \times \mathrm{HV}_{\mathrm{cell}} + Y_{\mathrm{Lig}} \times \mathrm{HV}_{\mathrm{Lig}} \tag{1}$$

where Y represents the mass fraction of different biomass components. The conversion of each of the biomass component (f_{k}) and the overall conversion (F) can be given as

$$f_k = \frac{m_k - m_{k,\mathrm{Char}}}{m_{k,o} - m_{k,\mathrm{Char}}} = \frac{Y_k - Y_{k,\mathrm{Char}}}{Y_{k,o} - Y_{k,\mathrm{Char}}} = \frac{\text{mass of } k \text{ that remains to be devolatilized}}{\text{Max mass of } k \text{ that could be devolatilized}}$$
$$k = \text{hemicellulose, cellulose and lignin.} \tag{2}$$

$$F = \frac{m}{m_0} = \frac{\sum m_k}{m_0} = \left\{f_k\left(Y_{k,o} - Y_{k,Char}\right) + Y_{k,Char}\right\} = \frac{\text{mass left over}}{\text{Initial mass}} \tag{3}$$

where $Y_k = m_k/m_0$: m_0 is the initial dry ash-free mass of the component, and $\mathrm{m_k}$ is the dry ash-free mass of component after time t. $Y_{k,\text{char}}$ represents the mass fraction of k remaining in char at end of pyrolysis. The energy content ratio of the biomass after being heat treated for some time period can be determined from the remaining mass fraction of each component k of the treated sample and heating value of individual components (Eq. 1).

Assuming first-order pyrolysis for each component k, the decomposition of each of the biomass component can be determined using the following:

$$-\frac{\mathrm{d}m_k}{\mathrm{d}t} = B_k m_k \exp\left(\frac{-E_k}{\bar{\mathrm{R}}\mathrm{T}}\right), \quad k = \text{Hemicellulose, Cellulose, Lignin} \tag{4}$$

where m_k is the mass remaining in each of the components in sample (kg) which can be devolatilized. $m_k = (m_{k,0} - m_{k,\text{char}}) - m_{k,\text{lib}}$. Amount of char in each of the components was obtained from the pyrolysis data available elsewhere (Yang et al. 2007).

$$\frac{\mathrm{d}m_{k,lib}}{\mathrm{d}t} = B_k\left(m_{k,0} - m_{k,\text{char}} - m_{k,\text{lib}}\right)\exp\left(\frac{-E_k}{\bar{\mathrm{R}}\mathrm{T}}\right) \tag{5}$$

The above expression can be further simplified to

$$\frac{\mathrm{d}\alpha_k}{\mathrm{d}t} = B_k(1 - \alpha_k)\exp\left(\frac{-E_k}{\bar{\mathrm{R}}\mathrm{T}}\right) \tag{6a}$$

$$\frac{\mathrm{d}\alpha_k}{\mathrm{d}T} = \left(\frac{B_k}{\beta}\right)(1 - \alpha_k)\exp\left(\frac{-E_k}{\bar{\mathrm{R}}\mathrm{T}}\right) \tag{6b}$$

where α represents the liberated fraction,

$$\alpha_k = \frac{m_{k,\text{lib}}}{m_{k,0} - m_{k,\text{Char}}} = \frac{m_{k,0} - m_k}{m_{k,0} - m_{k,\text{Char}}} = \frac{Y_{k,0} - Y_k}{Y_{k,0} - Y_{k,\text{Char}}} \tag{7}$$

When the sample is heated at a constant heating rate β, Eqs. 6a and 6b reduce to

$$f_k = (1 - \alpha_k) = \exp\left[-\left(\frac{B_k}{\beta}\frac{E_k}{\bar{R}}\right)\cdot\left\{\frac{\mathrm{E}_2(X_k)}{X_k} - \frac{\mathrm{E}_2\left(X_{k,0}\right)}{X_{k,0}}\right\}\right], \quad T < T_{\text{torr}} \tag{8}$$

where $\beta = \mathrm{d}T/\mathrm{d}t$ (Chen 2012). Once the torrefaction temperature T_{torr} is reached, the sample is maintained at T_{torr}, a constant value for a given residence time. From Eqs. (6a) and (6b), the mass loss during the constant temperature period for each of the component can be determined.

$$f_k = (1 - \alpha_k) = \exp\left\{ -B_k f_{k,T_{\mathrm{torr}}} \exp\left(\frac{-E_k}{\bar{R} T_{\mathrm{torr}}} \right) (\mathrm{t} - \mathrm{t}_{\mathrm{start,fixed\ T}}) \right\}, \quad T = T_{\mathrm{torr}} \tag{9}$$

where B_k is the pre-exponential rate constant, E_k the activation energy for the kth component, and $\overline{R}$ is the universal gas constant. The overall conversion (F) during the torrefaction process can be determined from the conversion of each biomass component (f_k) using Eq. (3).

2.4 Respiratory Quotient (RQ)

Considering a power plant producing a fixed amount of power, heat input from the fuel and oxygen consumption for most fuels are fixed. Hence, a fuel with higher RQ factor will result in more CO_2 being released into the environment. Fuel chemical composition can be used to determine the fuel heating value using an empirical relation given by Boie (Annamalai and Puri 2007).

$$\begin{aligned} \mathrm{HHV(kJ/kmol)} = {} & 422{,}270 \times \mathrm{C} + 117{,}385 \times \mathrm{H} - 177{,}440 \times \mathrm{O} + 87{,}985 \times \mathrm{N} \\ & + 335{,}510 \times \mathrm{S} \end{aligned} \tag{10}$$

where C, H, O, N, and S are the number of carbon, hydrogen, oxygen, nitrogen, and sulfur atoms, respectively, in the fuel. Stoichiometric oxygen needed for complete combustion of a $\mathrm{C_C H_H N_N O_O S_S}$ can be determined from the fuel chemical composition using the following relation.

$$\begin{aligned} v_{O_2}(\text{kg of oxygen/kg of fuel}) &= \frac{32 \times \left(\mathrm{C} + \frac{\mathrm{H}}{4} - \frac{\mathrm{O}}{2} + \mathrm{S}\right)}{M_{\mathrm{fuel}}} \\ &= \frac{32 \times \mathrm{C} \times \left(1 + \frac{\mathrm{H}}{4\mathrm{C}} - \frac{\mathrm{O}}{2\mathrm{C}} + \frac{\mathrm{S}}{\mathrm{C}}\right)}{M_{\mathrm{fuel}}} \end{aligned} \tag{11}$$

From Eqs. (10) and (11), Higher heating value of fuels per kg of stoichiometric oxygen ($\mathrm{HHV_{O_2}}$) can be determined. It was estimated that $\mathrm{HHV_{O_2}}$ calculated for all the fuels was around 14,000 kJ/kg O_2 (Annamalai and Puri 2007; Thanapal 2014).

Based on the fuel composition, RQ of a particular fuel with C atoms of carbon which can produce C moles of carbon dioxide can be determined using the following equation.

$$RQ = \frac{1}{\left\{1 + \left(\frac{H}{4C}\right) - \left(\frac{O}{2C}\right) + \left(\frac{S}{C}\right)\right\}} \tag{12}$$

3 Results and Discussion

3.1 Fuel Preparation and Properties

Biomass fuels used for the current study, mesquite and juniper, were harvested from the rangelands in north central Texas near Vernon. Both mesquite and juniper are scattered over a large area which is estimated to be 200,000 ha. It should be noted that the species is not concentrated throughout the entire area but dispersed with a spacing of around 1 km. After the fuel is harvested using a chainsaw, a chipper is used to reduce the particle size from trunk and branches. It also includes the bark. It was observed that, when a freshly harvested biomass (moisture content around 45 %) was sent into the chipper for reducing the particle size, the chips produced after the chipping process had a lower moisture percentage of between 10 and 20 %. This might be because of the drying of the wood chips within the chipper using the heat produced as a result of the chipping process. Vermeer wood chippers were used for processing the biomass. Further details on the preparation of the samples are available elsewhere (Chen 2012). Properties of mesquite and juniper obtained from the commercial testing labs are shown in Table 1.

Table 1 Ultimate and Proximate analyses of mesquite and juniper

	Raw biomass	
	Mesquite	Juniper
Moisture (ar)	15.53	5.85
Volatile matter (ar)	66.09	77.99
Fixed carbon (ar)	16.71	14.25
Ash (ar)	1.67	1.91
Carbon (ar)	43.60	49.27
Oxygen (ar)	33.57	37.00
Hydrogen (ar)	4.98	5.68
Nitrogen (ar)	0.62	0.28
Sulfur (ar)	0.03	0.01
Dry ash-free basis		
VM (daf)	79.8	84.6
FC (daf)	20.2	15.4
HHV (kJ/kg)	16,666	18,987
HHV_{dry} (kJ/kg)	19,730	20,167
HHV_{DAF} (kJ/kg)	20,128	20,584
VM HHV_{DAF} (kJ/kg)	16,923	18,351
$HHV_{Boie,DAF}$ (kJ/kg)	21,059	21,509
HHV (kJ/kg st O_2)	13,652	13,632

3.2 *Thermogravimetric Analysis*

3.2.1 Mesquite

The thermograms for pyrolysis and torrefaction of mesquite using N_2, Ar, and CO_2 as the purge are shown in Figs. 1 and 2. The TGA thermograms for each purge gas have the same relative shape and can be broken down into three different zones: drying, active pyrolysis zone, and passive pyrolysis zone. For simplicity, the thermograms for each torrefaction temperature were overlaid on the same plot. For torrefaction, each thermogram follows the weight loss curve for pyrolysis until reaching the torrefaction temperature. At this point, the thermogram follows a vertical line resulting from weight loss due to the sample being held at a constant temperature for the duration of torrefaction. Overlaying the thermograms of samples that were pyrolyzed and torrified using different purge gasses gives more insight as to the effect of the purge gas upon the breakdown of the biomass. Overlays of both argon and carbon dioxide versus nitrogen (the reference gas) are shown in Figs. 1 and 2, respectively, (Eseltine 2011).

From initial inspection, it is clear that there is very little difference in the thermograms from the pyrolysis and torrefaction in nitrogen and argon. Both nitrogen and argon exhibit roughly the same amount of weight loss at a given torrefaction temperature. Slight differences in weight loss between these two purge gases can be attributed to differences in the biomass samples being tested. Comparison of the thermograms using nitrogen and carbon dioxide as the purge gas shows a noticeable difference between the two gases. For torrefaction temperatures above 240 °C, samples torrefied using CO_2 as the purge gas have a higher amount of weight loss

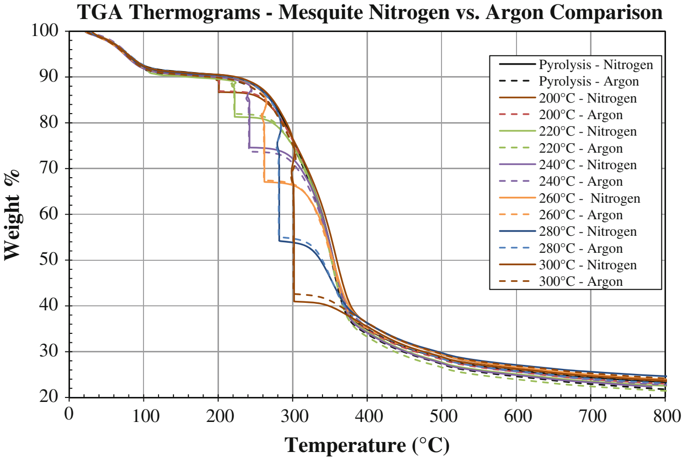

Fig. 1 Comparison of thermograms from pyrolysis and torrefaction of mesquite wood using N_2 and Ar as the purge gases, adapted from Eseltine (2011)

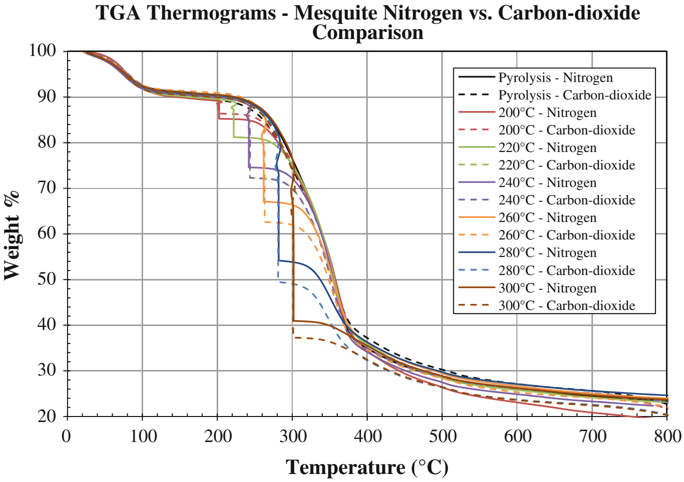

Fig. 2 Comparison of thermograms from pyrolysis and torrefaction of mesquite wood using N_2 and CO_2 as the purge gases, adapted from Eseltine (2011)

than samples torrefied using nitrogen. This is due mainly to chemical reactions occurring between CO_2 and the carbon within the fuel which will be discussed in further detail in a subsequent section.

3.2.2 Juniper

Data obtained from torrefaction and pyrolysis of juniper wood chips were analyzed in the same manner as the data from mesquite wood pyrolysis and torrefaction. The shape of the thermograms from juniper wood follows the same trends as the thermograms from mesquite wood. The only noticeable difference between the pyrolysis curves of mesquite and juniper is being the weight percent remaining after the active pyrolysis zone. Juniper wood loses more weight during the initial active pyrolysis zone when compared to mesquite due to differences in the chemical composition of the two biomasses.

Comparing the weight loss from the torrefaction of mesquite and juniper wood, it can be seen that mesquite wood has a higher amount of weight loss at a given torrefaction temperature. This is due mainly to differences in the chemical composition of both biomasses. Prins et al. (2006a) have stated that deciduous woods, such as mesquite, have a hemicellulose fraction comprised of mostly xylan. Xylan is being more reactive than mannan, the main constituent of the hemicellulose fraction found in coniferous woods (such as juniper). Due to the temperature range over which hemicellulose breaks down, a significant portion of the weight lost during torrefaction occurs from the decomposition of hemicellulose. Therefore, the hemicellulose fraction of mesquite being more reactive than that of juniper is the main cause for a higher weight loss during the torrefaction of mesquite.

For further analysis of the effect of the purge gas upon the torrefaction of juniper, thermograms from the torrefaction and pyrolysis using argon and carbon dioxide were overlaid with the thermograms using nitrogen as the purge gas. These overlays can be seen in Figs. 3 and 4, respectively. The trends observed from the comparison of argon and carbon dioxide to nitrogen appears similar to the ones observed from

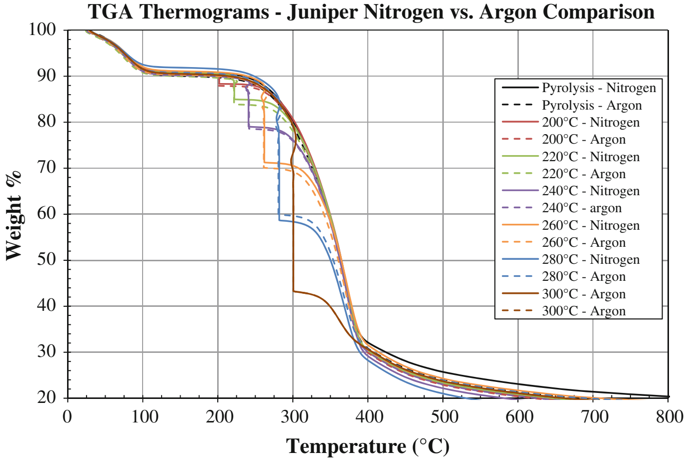

Fig. 3 Comparison of thermograms from pyrolysis and torrefaction of juniper wood using N_2 and Ar as the purge gasses, adapted from Eseltine (2011)

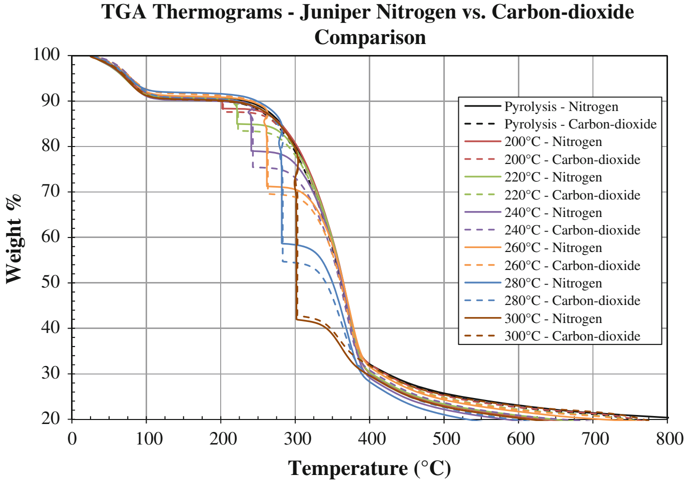

Fig. 4 Comparison of thermograms from pyrolysis and torrefaction of juniper wood using N_2 and CO_2 as the purge gases, adapted from Eseltine (2011)

previous experiments with mesquite. The slight differences are attributed to the variations in the samples tested. Comparison of the thermograms using nitrogen and carbon dioxide as the purge gas shows that using carbon dioxide results in a higher amount of weight loss.

3.2.3 Optimum Torrefaction Temperature

Based upon the TGA thermograms, an optimal torrefaction temperature can be determined. From the TGA thermograms presented for each biomass and purge gas at 240 °C, more than 70 % of the initial mass of the biomass remains after torrefaction. This is independent of both biomass and purge gas. Tests conducted at a torrefaction temperature of 260 °C resulted in roughly 58–65 % of the biomass remaining. Furthermore, an estimated percent of energy retained after torrefaction can be calculated based upon the raw biomass fuel properties and the TGA weight traces. The energy retention estimates were calculated based upon the HHV of the fuel on a dry ash-free (DAF) basis and the amount of fixed carbon (FC) and volatile matter (VM) in the biomass. If we use the DAF HHV of the biomass, the energy content comes entirely from the VM and FC and the following relation can be used.

$$\mathrm{HHV_{DAF}}\left(\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = \mathrm{HHV_{VM}} \times \mathrm{VM} + \mathrm{HHV_{FC}} \times \mathrm{FC} \tag{13}$$

If we assume that the mass lost during torrefaction is entirely due to liberation of volatiles then the HHV of the torrefied biomass can be estimated as

$$\mathrm{HHV_{DAF,TB}}\left(\frac{\mathrm{kJ}}{\mathrm{kg}}\right) = (\mathrm{wt\%} \times \mathrm{VM} \times \mathrm{HHV_{VM}}) + (\mathrm{HHV_{FC}} \times \mathrm{FC}) \tag{14}$$

where wt% represents the weight remaining after torrefaction. Using the estimation proposed above to determine the HHV of the torrefied biomass on a DAF basis, it is possible to estimate the amount of energy retained after torrefaction using the following relation (Eseltine 2011).

$$\text{Energy Retained } (\%) = \left(\frac{M_{\mathrm{TB}} \times \mathrm{HHV_{TB}}}{M_{\mathrm{RB}} \times \mathrm{HHV_{RB}}}\right) \times 100 \tag{15}$$

Using data from the heat value analysis of the raw biomass, which gives the HHV of the VM, with the proximate analysis results an estimated HHV of the torrefied biomass can be calculated and therefore an estimated energy retained %. Based upon the mass loss observed from TGA thermograms as well as the estimated energy retention calculations, the optimal torrefaction temperature was determined to be 240 °C. For all of the biomass tested in each purge gas environment, torrefaction at 240 °C results in over 85 % energy retention as well as 70 % of the initial mass remaining.

3.2.4 Laboratory Oven Tests

After determining the optimal torrefaction temperature, large samples of each biomass were torrefied in a laboratory oven using nitrogen, argon, and carbon dioxide as the purge gas. Torrefied samples were then sent to commercial testing labs for analysis. Figure 5 shows the properties of the raw and torrefied samples. As expected, torrefaction of the raw biomass resulted in reduced moisture content in the biomass. Torrefaction of raw biomass also resulted in an increased ash and fixed carbon content for all biomass tested. The increase in ash and FC is mostly due to the decrease in moisture content and liberation of light weight volatiles during torrefaction. Biomass torrefied in an argon or nitrogen environment exhibits little difference in fuel properties. However, the fuel properties of biomass torrefied in carbon dioxide are slightly different.

Previous research (Lawrence et al. 2009) has shown that coal–biomass blends with a ratio of coal to biomass greater than 80:20 result in several combustion issues due to the fuel properties of the raw biomass. With the fuel properties of torrefied biomass being much better than raw biomass, it is entirely feasible that blended fuels with a ratio of coal to torrefied fuel greater than 80:20 could be used in co-firing applications.

Knowing the actual HHV of the torrefied biomass (HHV_{TB}), the actual amount of energy retained can be calculated (Sect. 3.2.3). Due to inherent mass loss from torrefaction, the energy retained provides the percentage of the raw biomass retained within the torrefied biomass. The resulting calculated values of energy retained for both biomasses in each purge gas environment can be seen in Table 2.

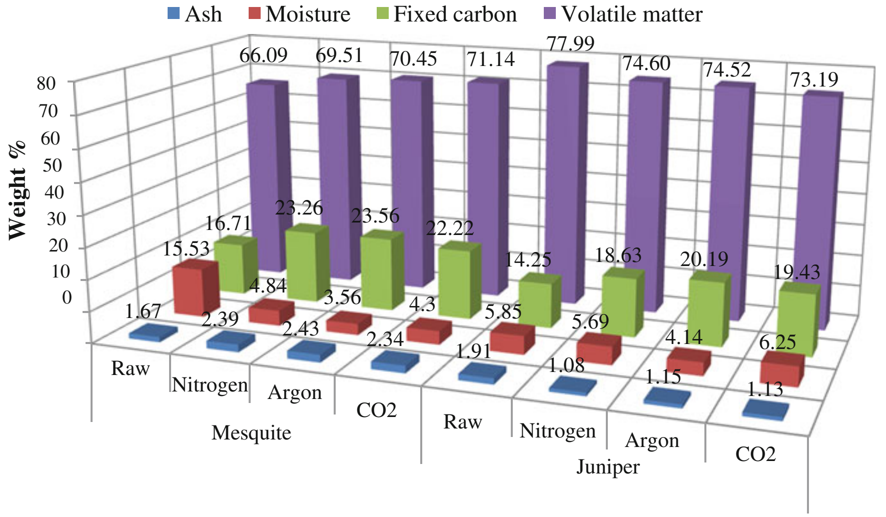

Fig. 5 Proximate analysis of raw and biomass torrefied using different mediums (Eseltine 2011)

Table 2 Percent energy retained in the torrefied biomass

Biomass	Purge gas		
	Nitrogen	Argon	Carbon dioxide
Mesquite	88.74	87.73	84.47
Juniper	83.68	83.16	78.86

The energy retention calculations show that torrefaction in a nitrogen environment resulted in the highest amount of energy being retained. Torrefaction using argon as the purge gas had a slightly lower amount of energy retention when compared to nitrogen. However, the energy retention of torrefaction in a carbon dioxide environment shows that using carbon dioxide as a purge gas results in the lowest energy retention for all three biomasses tested. The lower amount of energy being retained after torrefaction using CO_2 is a result of more volatiles being liberated via the Boudouard reaction.

3.2.5 Grindability Tests

The samples torrefied using the laboratory oven were then ground using an in-house vibratory grinding mill. From the grindability tests, torrefied samples exhibited improved grindability in comparison to raw biomass samples. For both mesquite and juniper, torrefaction using CO_2 resulted in a higher fraction of the ground biomass passing through an 840-μm mesh size. Further grindability tests conducted on samples torrefied in a bigger batch reactor by Thanapal et al. showed that using CO_2 as the torrefaction improved the grindability of torrefied samples by 30 %. More details on those tests are available elsewhere (Eseltine 2011).

3.2.6 Torrefaction Model

Properties of the Biomass Components

The ultimate and proximate analyses of mesquite and juniper are presented in Table 1. In addition, ultimate and proximate analyses of hemicellulose and cellulose were obtained from literature (Yoon et al. 2011; Van de Weerdhof 2010). The composition of lignin was then determined from the fuel composition and the data for hemicellulose and cellulose according to Eq. (1). Composition of cellulose and hemicellulose is presented in Table 3.

Based on the pyrolysis tests carried out on the three components, 32, 2.5, and 40 %, were left over as char from hemicellulose, cellulose, and lignin, respectively, on a dry ash-free basis (Raveendran et al. 1996). The estimated bulk char percentage on a DAF% based on the percentage of hemicellulose, cellulose, and lignin (Table 3) and the char content left after pyrolysis will be 15.64 and 17.44 % for hard wood mesquite and softwood juniper samples, respectively. The numbers

Table 3 Ultimate and proximate analyses of biomass components (Van de Weerdhof 2010; Yoon et al. 2011)

	Hemicellulose	Cellulose
Volatile matter (db)	74.11	91.64
Fixed carbon (db)	21.94	8.54
Ash (db)	3.95	0
C (daf)	43.77	43.58
H (daf)	5.91	6.09
O (daf)	50.26	50.27
N (daf)	0.05	0.05
S (daf)	0.02	0.01
Heating value (kJ/daf kg)	15,920	17,870

estimated for the bulk char percentage in the two samples were similar to the fixed carbon in mesquite and juniper on a dry ash-free basis (16.98 % for mesquite and 15.45 % for juniper from Table 2). The percentage of fixed carbon in the three components was used as a reference to determine the amount of volatile matter released from the components during the torrefaction process. Amount of these three components depends on the type of biomass. Hardwood was found to contain higher percentage of hemicellulose when compared to softwood. Percentage of the different components in hardwood and softwood was obtained from Liu et al. (2008). Table 4 shows the percentage of the three components along with the kinetic constants for the three components which were determined using error minimization technique.

Component Conversion and Mass Loss During Torrefaction: TCM

Volatilization of the three components at different torrefaction temperatures and residence times was studied. The results obtained for torrefaction of mesquite which is a hardwood at 240 °C for a residence time of 60 min is shown in Fig. 6. It was assumed that the samples are heated from room temperature to the desired torrefaction temperature at a heating rate of 20 °C/min.

Table 4 Composition of hardwood and softwood

	Hemicellulose (%)	Cellulose (%)	Lignin (%)
Softwood (Liu et al. 2008)	12.27	53.26	26.66
Hardwood (Liu et al. 2008)	28.97	53.95	9.43
B (1/min)	6.66E+08 (Cozzani et al. 1997)	6.83E+16 (Orfao et al. 1999)	1,000 (Varhegyi et al. 1997)
E (kJ/mol)	103.2 (Cozzani et al. 1997)	201 (Orfao et al. 1999)	65 (Varhegyi et al. 1997)

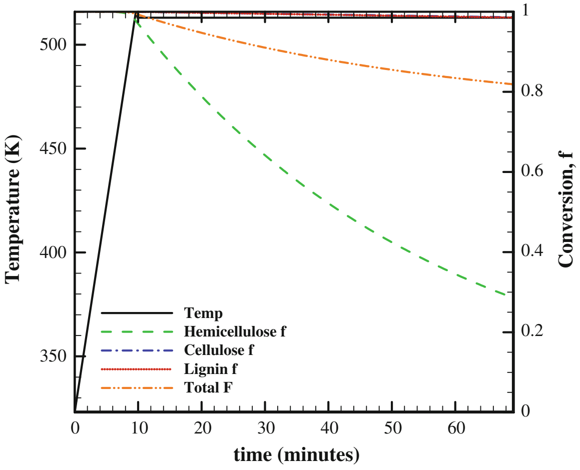

Fig. 6 Torrefaction of mesquite at 240 °C for 60 min: results predicted by TCM

The loss of volatiles from the three components of mesquite after 60-min time period at 240 °C was predicted to be 71.5, 1.39, and 1.46 % for hemicellulose, cellulose, and lignin, respectively, on a dry ash-free basis. The overall dry ash-free mass loss from the biomass sample was 18.1 %. The results obtained from previous torrefaction experiments carried out on smaller samples (10 mg) in a TGA on a dry ash-free basis were used as a reference for comparison with model results. It should also be noted that the juniper which is a softwood shows lower mass loss due to lower percentages of hemicellulose in the sample.

Effect of temperature on the torrefaction process was studied using TCM. Figure 7 compares the TCM results with the experimental results for a residence

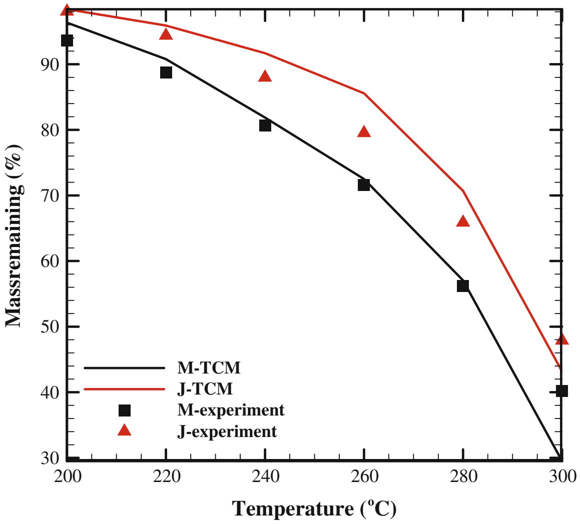

Fig. 7 Effect of temperature on the loss of volatile matter from the samples. Results from the model are compared with experimental results. *M* Mesquite; *J* Juniper; *TCM* Three-component model; t_{res} = 60 min

time of 60 min for both mesquite and juniper samples. The model results compare well with the experimental results except at the upper temperature limit. At temperature of 300 °C, TCM overpredicts the mass loss from the woody biomass. The kinetic constants of cellulose used to model the torrefaction process resulted in increased losses of cellulose at higher temperatures in the TCM. The variation in mass loss with increase in residence time for an initial heating rate of 20 °C/min is plotted in Fig. 8. Following residence times were studied: 30, 45, 60, and 120 min. Effect of higher residence time on mass loss was negligible at lower torrefaction temperatures, while an increase in temperature resulted in increased mass loss due to higher time and energy available for the volatilization of cellulose and lignin present in the biomass. Higher percentages of cellulose are released from the sample resulting in higher mass loss.

As the heating rate increased, the results showed an increased retention of mass at higher torrefaction temperatures when compared to the lower heating rates. Higher heating rates do not allow sufficient time for the volatiles to escape out from the biomass which causes lower mass loss during the initial heat up period. Hence, higher heating rates can be employed to reduce the loss of combustible volatile matter from the biomass at higher temperatures.

Energy Conversion Ratio (ECR) and Heating Value of the Torrefied Sample

The heating value and the chemical composition of the three components were used to monitor the change in heating value of the torrefied biomass with reference to the raw samples. Energy conversion ratio (ECR) which is defined as the ratio of the energy content of the torrefied sample to the energy content of the raw biomass and the ratio of the heating value of the torrefied biomass to raw biomass was also

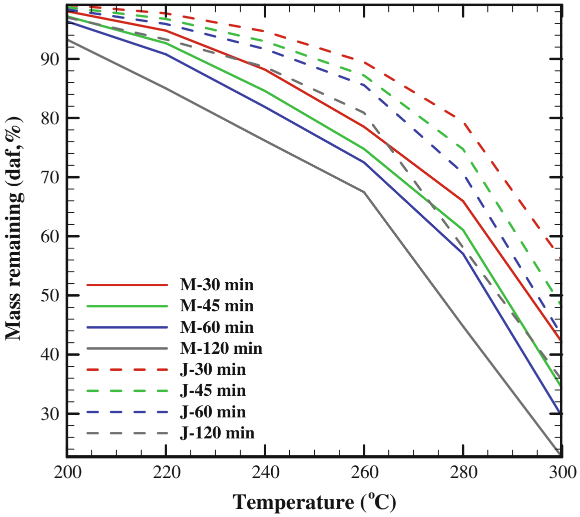

Fig. 8 Variation in mass loss with increase in torrefaction temperature and residence times. *M* Mesquite; *J* Juniper

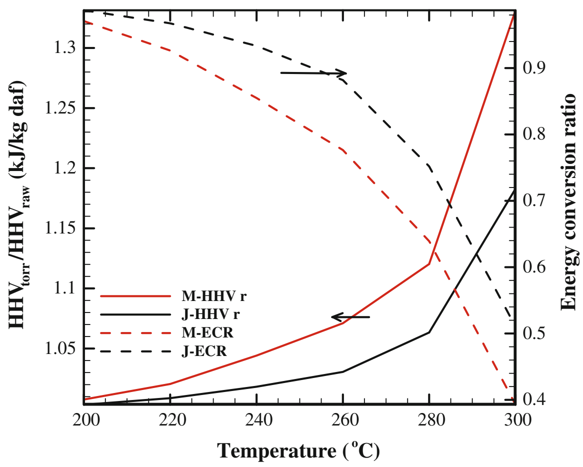

Fig. 9 Variation in heating value and ECR with increase in temperature. *M* Mesquite; *J* Juniper; *HHV r* Heating value ratio; *ECR* Energy conversion ratio

determined. Figure 9 shows the variation of heating value and ECR with respect to torrefaction temperatures.

As can be observed from Fig. 9, heating value of the torrefied sample increases with increase in torrefaction temperature as the hemicellulose and cellulose volatilizes and the sample becomes rich in char and lignin which have higher heating value. The ratio of the heating value of the torrefied samples to the raw biomass samples from the experiments at 240 °C for a residence time of 60 min was 1.06 and 1.05 for mesquite and juniper, respectively. The ratio of the heating values predicted by the model was lower. In the case of TCM, the composition of volatile matter released from the sample is assumed to remain constant and it also includes carbon and hydrogen along with oxygen. Hence, lower ratios were predicted by the model when compared to that of experiments. The ECR of the torrefied samples decreases due to loss of combustible volatile matter. As the energy content of the sample decreases with increase in temperature, ECR decreases. It is seen that ECR decreases rapidly after about 260 °C due to higher loss of cellulose. Thus, T_{torr} must be limited to $T_{torr} < 260$ °C. However, on a unit mass basis, heating value of the torrefied sample is higher than the raw biomass. Hence, the three-component model is a simple and powerful model to predict the mass loss from the biomass samples undergoing torrefaction. Such a model can also be applied to the fibrous biomass torrefaction. It should be noted here that the order of reaction for the volatilization of the three components is assumed to be one.

The kinetics used in the TCM also influences the amount of mass loss and change in heating value of the sample. In order to compare the effect of kinetic constants on the mass and energy yield, kinetics of pine wood components extracted using error minimization technique (Wang et al. 2012b) was used to predict the mass loss and ECR. The results obtained were compared to the heating value ratio determined using the kinetics presented in Table 4. Figure 10 plots the

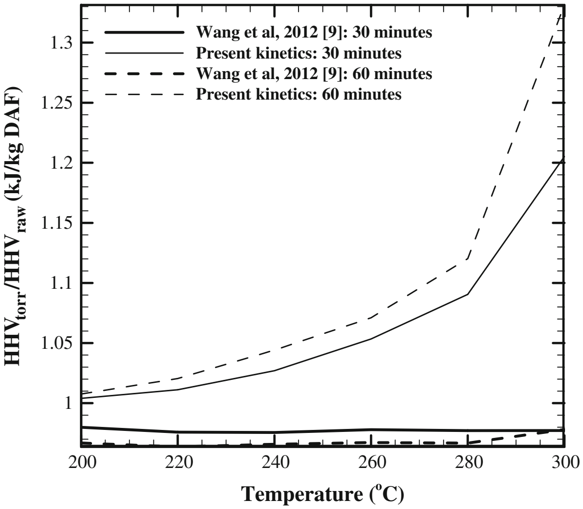

Fig. 10 Variation in heating value with increase in torrefaction temperatures for two different kinetics. (i) Kinetics obtained from Wang et al. (2012b) and (ii) kinetics from Table 4

variation in heating value ratios obtained for two different residence times. Kinetics obtained from Wang et al. (2012b) resulted in higher losses in Lignin which decreased the heating value of the torrefied samples.

3.3 *RQ Factor for Fuels*

3.3.1 CO_2 Emissions

Boie equation can be used to derive an expression to estimate the CO_2 emitted in tons per GJ of energy input from the fuel chemical composition as given in the Eq. (16).

$$\mathrm{CO_2 in\ tons/GJ} = \frac{1 \times 44 \times 1{,}000}{\left\{422{,}270 \times \left(1 + \left(\frac{117{,}385}{422{,}270}\right) \times \left(\frac{\mathrm{H}}{\mathrm{C}}\right) - \left(\frac{177{,}440}{422{,}270}\right) \times \left(\frac{\mathrm{O}}{\mathrm{C}}\right)\right)\right\}} \tag{16}$$

The CO_2 in tons per GJ of energy input is given according to Eq. (17a) (Thanapal 2014).

$$\mathrm{CO_2\ in\ tons\ per\ GJ\ energy\ input} = \mathrm{RQ} \times \frac{\mathrm{kg\ O_2}}{\mathrm{HHV_{O_2}\ in\ GJ}} \times \frac{\mathrm{kmol\ O_2}}{\mathrm{32\ kg}} \times \frac{\mathrm{44.01\ kg}}{\mathrm{kmol\ CO_2}} \times \frac{\mathrm{0.001\ tons}}{\mathrm{kg}} \tag{17a}$$

Assuming $\mathrm{HHV}_{\mathrm{O}_2} = 0.014$ GJ/kg O_2,

$$\mathrm{CO}_2 \text{ in tons per GJ of energy input can be reduced to} \approx \mathrm{RQ} \times 0.1. \qquad (17\mathrm{b})$$

where the approximate sign is due to assumption of constant $\mathrm{HHV}_{\mathrm{O}_2} = 0.014$ GJ per kg of O_2 consumed. For RQ = 1 (pure carbon), CO_2 is about 0.1 tons per GJ or 100 g per MJ.

In order to validate approximate expression for CO_2, actual measured heating values of fuels for which compositions are well known (e.g., CH_4, $\mathrm{C}_8\mathrm{H}_{18}$, $\mathrm{C}_{12}\mathrm{H}_{23}$, $\mathrm{C}_2\mathrm{H}_5\mathrm{OH}$, coal, and biomass) are used to estimate CO_2 in tons per GJ. Results are shown in Fig. 11. It is apparent from Fig. 11 that CO_2 in tons per GJ of energy input has a slope of 0.1 which confirms the approximation.

The RQ factor for fuels of known composition can be estimated using Eq. (12). Table 5 shows the variation of RQ factor for different fuels.

In general, the RQ factor increases with decrease in hydrogen-to-carbon ratio. Methane which has a H/C ratio of 4 has the lowest RQ factor for pure fuels with RQ = 0.5. It can be observed from Table 5 that the solid fuels have comparatively higher oxygen content. Higher oxygen content results in higher RQ factor for solid fuels. Gasoline and diesel fuels which are used in the automobiles have a comparatively lower RQ when compared to that of solid fuels. Lower O/C ratio of the liquid fuels is one of the factors behind the lower RQ values.

It is seen that most solid fuels (pure carbon RQ = 1, biomass fuels (mesquite and juniper) RQ = 0.94–0.97, most sweet sorghum sources = 0.98–1.0 (TAMU 2013),

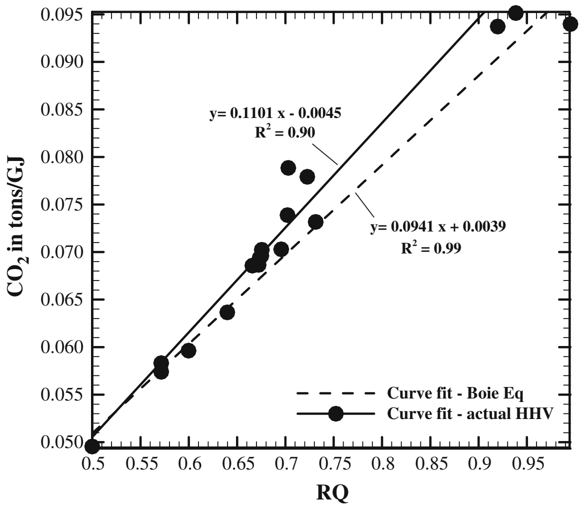

Fig. 11 CO_2 emitted in tons per GJ of energy input for fuels with different RQ factors. Fuel measured heating value and composition data was used in estimation of CO_2. Slope of both the trend lines (actual heating value and heating value estimated using Boie equation) was 0.1 which is same as the approximate value derived using Eq. (17b)

Table 5 RQ factor for different fuels along with their respective O/C and H/C ratios

Fuel	O/C	H/C	*RQ*
Gaseous fuels			
Methane	0.00	4.00	0.50
Ethane	0.00	3.00	0.57
Ethylene	0.00	3.00	0.57
Propane	0.00	2.67	0.60
Acetylene	0.00	1.00	0.80
Liquid fuels			
Methanol[a]	1.00	4.00	0.67
Ethanol[a]	0.50	2.99	0.67
Gasoline (C_8H_{18})	0.00	2.25	0.64
Diesel ($C_{12}H_{23}$)	0.00	1.92	0.68
Biodiesel[a]	0.10	1.90	0.70
Free fatty acid from peanut oil soap stock[a]	0.07	1.83	0.70
Canola oil[a]	0.08	1.63	0.73
Heavy oil	0.01	1.55	0.72
Bio oil (wood pyrolysis)[a]	0.50	1.34	0.92
Solid fuels			
Softwood (juniper)[a]	0.56	1.39	0.94
Hardwood (mesquite)[a]	0.58	1.37	0.95
Fibrous (rice straw)[a]	0.66	1.33	1.00
Animal based (LAPCDB)[a]	0.40	1.26	0.89
WYO coal	0.18	0.70	0.92
TXL coal	0.19	0.68	0.93

[a] Renewable fuels

coals RQ = 0.92–0.93, and animal wastes RQ = 0.92–0.95) have a RQ factor of around 0.95. Gaseous and liquid fuels have RQ between 0.50 and 0.80. It is noted that renewable biomass fuels have slightly higher RQ (e.g., coal with RQ of 0.92 and biomass with RQ of 0.97).

Figure 12 shows the plot for variation of "RQ" with H/C and O/C ratio of the fuels. Since HHV_{O_2} is constant for most fuels, then for given thermal input, the O_2 mol consumed will remain the same. Hence, a fuel with higher RQ produces more CO_2 for same thermal heat input, i.e., more tons of CO_2 per GJ. RQ scaling is applied only to oxidation processes, for example, RQ tends to ∞ for anaerobic digestion which produces CH_4 and releases CO_2 since no O_2 is consumed. It does not imply that it has highest global warming potential. Here, the production of CH_4 becomes important. Even in human body, senior people seem to have a higher RQ compared to young adults (Rizzo et al. 2005) due to anaerobic digestion in O_2 starved cells.

Using the Boie equation, one can estimate the amount of carbon emissions from a fuel. Carbon dioxide emitted on a mass basis (g/MJ or kg/GJ) determined for

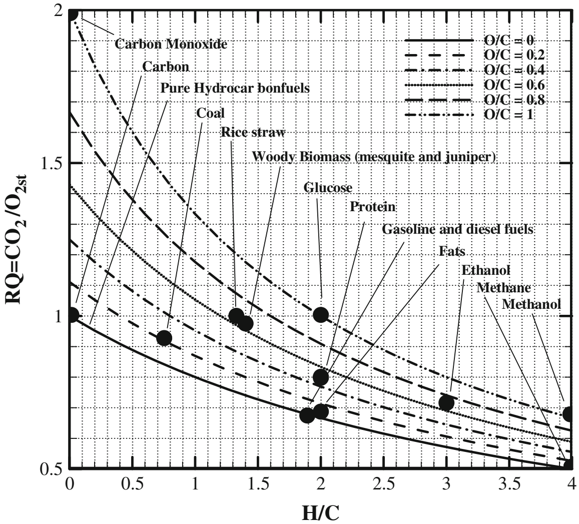

Fig. 12 Variation of RQ with H/C ratio and O/C ratio of the fuel. Gaseous and liquid fuels have lower RQ factor when compared to that of solid fossil and renewable fuels (Thanapal 2014)

different fuel compositions is shown in Fig. 13. Just as Environmental Protection Agency (EPA) sets limit on NO_x in lb per mmBTU or kg /GJ, the CO_2 amount must be estimated in kg per unit GJ or lb per mmBTU rather than kg of CO_2 per kg fuel since heat input must be maintained the same, when fuel is switched. Both Figs. 12 and 13 follow the same trend in terms of increased emissions with increase in oxygen content and C/H ratio in the fuel. From results on RQ factor and carbon dioxide emissions from fuels, it can be seen that the liquid fuels currently used in automobiles have the least RQ factor next only to natural gas. Biofuels produced from renewable energy sources are limited by the energy density and oxygen content.

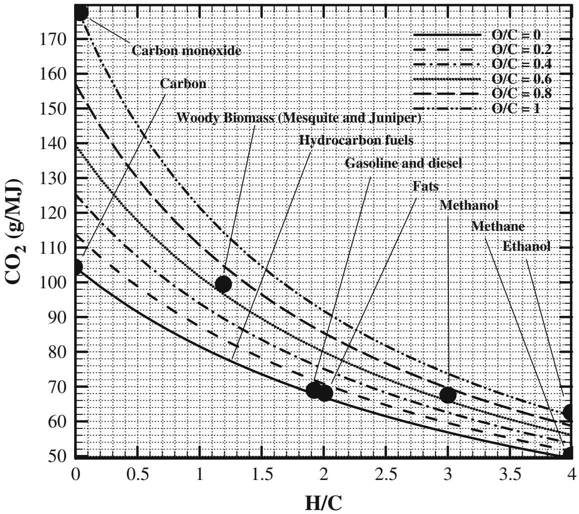

Fig. 13 Effect of H/C and O/C on the CO_2 emission from fuels. Fuels with higher RQ factor emit higher amounts of carbon dioxide

If the oxygen content can be reduced by using torrefaction of biomass, catalytic cracking, and hydrotreating (Jacobson et al. 2013) of bio-oils, the energy density of the biomass and bio-oils can be improved and in turn will also reduce the RQ factor of the fuels. But such a process also reduces the yield of bio oil. Though renewable fuels are argued to be carbon neutral, their potential to emit carbon is much higher (higher RQ when compared to coal). Coupled with its lower energy density, variability in production and process efficiencies and land usage pattern, studies should be done to effectively use fossil fuels with reduced RQ factor.

3.3.2 RQ Factor for Fuel Processing

Even though biomass is a renewable fuel where CO_2 produced by direct combustion is neutralized by CO_2 used in production of fuel, the processing of biomass (electrical power for pumping water, heat required for drying, fertilizer used for cultivation, fuels used for collection and transportation, etc.) releases CO_2 if fossil fuels are used to grow and process biomass. Then, one can define equivalent RQ value ($\mathrm{RQ}_{\mathrm{process,biomass}}$) for biomass processing by estimating tons of CO_2 released per GJ of heat content of biomass delivered to power plants. $\mathrm{RQ}_{\mathrm{process,biomass}}$ can be defined according to Eq. (18) (Thanapal 2014).

$$\mathrm{RQ}_{\mathrm{process,biomass}} = 219 \times \frac{\mathrm{RQ}_{\mathrm{biomass}}}{\left(\frac{\mathrm{C\%}}{12.01}\right)} \left\{ \frac{\mathrm{RQ}_1 \times p_{\mathrm{elec.}}\left(\frac{\mathrm{GJ}}{\mathrm{kg\ biomass}}\right)}{\eta} + \frac{\mathrm{RQ}_2 \times q_{\mathrm{heat}}\left(\frac{\mathrm{GJ}}{\mathrm{kg\ biomass}}\right)}{\eta_{\mathrm{burner}}} + \mathrm{RQ}_3 + \mathrm{RQ}_4 \right\} \tag{18}$$

where RQ_1 refers to fossil fuel used for electric power generation, RQ_2 refers to another fossil fuel used for direct heat production, η: power plant efficiency, η_{burner}: burner efficiency, RQ_3 refers to CO_2 released during collection and transportation, RQ_4 for CO_2 produced while producing fertilizers and C%, carbon mass% in biomass fuels. RQ (by direct oxidation) is relatively fixed for most biomass fuels. However, C% decreases when there is more oxygen, moisture, and ash in biomass fuel. Thus, higher amount of biomass would be needed for the same heat input and larger the CO_2 emitted during the processing of renewable biomass fuels. Hence, $\mathrm{RQ}_{\mathrm{process,biomass}}$ increases and if it reaches same as coal, then such a biomass is not useful as renewable fuel, i.e., criteria must be $\mathrm{RQ}_{\mathrm{process,biomass}} < \mathrm{RQ}_{\mathrm{coal}}$ if biomass is used to replace coal in order to reduce GWP. Lifecycle assessment of willow biomass production was analyzed by Heller et al. (2003). Based on the analysis, it was estimated that the total energy consumed for the production of willow based biomass was 98.3 GJ/ha over seven harvest rotations. Around 13.6 oven dry tonnes per hectare per year was estimated to be the average yield of the biomass. Assuming mesquite and juniper will also consume similar amount of energy when cultivated on a large scale solely for the utilization of these woody biomass for power production, $\mathrm{RQ}_{\mathrm{process,biomass}}$ can be determined based on the data provided by Heller et al. (2003). The $\mathrm{RQ}_{\mathrm{process,biomass}}$ for both mesquite and juniper was found to be 0.03 based on the lifecycle analysis data. Further, when the raw biomass is torrefied, moisture content in the torrefied samples will be low. In addition to lower moisture content, torrefied samples will exhibit improved grindability. Hence, $RQ_{process,biomass}$ for the torrefied samples will be lower than the raw biomass samples.

3.3.3 RQ Factor for Fuel Blends

The RQ factor for the blend of biomass with coal should be less than the RQ factor for pure coal so that using biomass will result in reduced CO_2 emissions. RQ for the fuel blend can be determined using the following formula (Thanapal 2014).

$$RQ_{fuel,blend} = RQ_{coal} \times HF_{coal} + \left(RQ_{biomass} + RQ_{process,biomass}\right) \times HF_{biomass} \quad (19)$$

where HF is the heat fraction contributed by the fuel present in the blend. Heat fraction of a fuel is defined as the ratio of heat content of a particular fuel to the total heat content of the blend (kJ of fuel/kJ of fuel blend). For the case of 90:10 blends of coal and woody biomass which was used in the current study, the $RQ_{fuel,blend}$ was determined to be 0.82 assuming $RQ_{biomass}$ to be zero since biomass is considered carbon neutral. RQ factor for the fuel blend is lower than the coal RQ value which is 0.92. This indicates lower amount of CO_2 will be released into the atmosphere when 10 % of biomass on mass basis is blended with coal. Table 6 shows the RQ_{blend} for the different biomass blends which were used in the current study.

Further, it can be seen from Table 6 that the RQ_{blend} for coal and torrefied biomass is lower (0.82) than the raw biomass blends (0.84). Higher heat values of torrefied biomass resulted in higher heat fraction for biomass which led to lower numbers for RQ_{blend}. Also it should be noted that energy consumed for processing torrefied biomass will be lower than the raw biomass if hot flue gas from boiler is used for torrefaction.

Table 6 RQ factor for the 90:10 blends of coal and biomass on a mass basis (Thanapal 2014)

Fuel	RQ_{coal}	HF_{coal}	$RQ_{biomass}$	$RQ_{biomass,processing}$	$HF_{biomass}$	RQ_{blend}
PRB + RM	0.92	0.91	0	0.03	0.09	0.84
PRB + RJ	0.92	0.90	0	0.03	0.10	0.83
PRB + TM	0.92	0.89	0	0.03	0.11	0.82
PRB + TJ	0.92	0.89	0	0.03	0.11	0.82

HF Heat fraction; *PRB* Powder river basin sub-bituminous coal; *RM* Raw mesquite; *RJ* Raw juniper; *TM* Torrefied mesquite; *TJ* Torrefied juniper

4 Summary and Conclusion

The use of nitrogen and argon as a purge gas during the torrefaction of the two biomass tested produced the same results. Torrefaction of mesquite and juniper using carbon dioxide as the purge gas resulted in a higher weight loss. The higher amount of weight loss when using CO_2 can be attributed to the reaction of the CO_2 purge gas with fixed carbon contained within the biomass.

Overall, the use of carbon dioxide as a torrefaction medium results in a biomass with a smaller HHV than the same biomass torrefied in nitrogen or argon. Therefore, given the higher amount of weight loss with CO_2 and the smaller HHV, the amount of energy retained in the torrefied biomass is lowest when torrefying in a CO_2 environment. However, grindability studies show that biomass that is torrefied in a CO_2 environment is easier to grind than biomass torrefied in N_2. That is biomass torrefied in a CO_2 environment will require less energy to pulverize.

Considering all of these factors, it is suggested that carbon dioxide is a better torrefaction medium than nitrogen and argon. Although, higher weight losses and more moisture absorption were observed when using CO_2, the increased grindability and possibility that less energy would be required to produce high-quality fuel make CO_2 the better torrefaction medium.

A simple TCM based on independent parallel reactions has been developed to model the torrefaction of woody and fibrous biomass in order to predict mass loss, heating value of biomass at any stage of torrefaction versus temperature (or time). Mass loss predicted by the TCM was compared with the experimental data obtained from TGA. It is shown that heat value of the torrefied biomass increased with increase in pretreatment temperatures, while the energy retention ratio decreased at high temperatures due to loss of higher amounts of combustible volatile matter at higher temperatures.

Chemical composition of the fuels and correlations developed to estimate the heating values can be used effectively to study the variation in heating values with respect to the fuel properties. The RQ term defined as the amount of CO_2 mol produced per unit mole O_2 consumed used extensively in the biological literature has been applied to combustion applications. RQ factor has been used to estimate the amount of CO_2 which is a measure of GWP. Lower the RQ, lower the amount of CO_2 produced for every mole of oxygen consumed for combustion process and lower the CO_2 in tons per GJ which is shown to be approximately equal to 0.1 times RQ.

Further, a term called $RQ_{process,biomass}$ is introduced to determine the effect of using a renewable fuel along with fossil fuels. $RQ_{process,biomass}$ for both mesquite and juniper (which does not use water or electricity for cultivation) was estimated to be 0.03 based on woody biomass lifecycle analysis. Method for estimating the RQ_{blend} for the blend of coal and biomass was presented, and the RQ_{blend} for 90:10 blends of coal and torrefied biomass was 0.82 (where RQ for biomass is zero) which is lower than the RQ factor of raw coal which is 0.92.

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References

Almeida G, Brito JO, Perré P (2010) Alterations in energy properties of eucalyptus wood and bark subjected to torrefaction: the potential of mass loss as a synthetic indicator. Bioresour Technol 101:9778–9784

Annamalai K (2013) Respiratory quotient (Rq), exhaust gas analyses, CO_2 emission and applications in automobile engineering. Adv Automobile Eng 2(2):e116

Annamalai K, Puri IK (2007) Combustion science and engineering. CRC Press, Boca Raton

Antal MJJ, Varhegyi G (1995) Cellulose pyrolysis kinetics: the current state of knowledge. Ind Eng Chem Res 34:703–717

Anthony DB, Howard JB, Hottel HC, Meissner HP (1976) Rapid devolatilization and hydrogasification of bituminous coal. Fuel 55:121–128

Arias B, Pevida C, Fermoso J, Plaza MG, Rubiera F, Pis JJ (2007) Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Process Technol 89(2):169–175

Arias B, Pevida C, Fermoso J, Plaza MG, Rubiera F, Pis JJ (2008) Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Process Technol 89:169–175

Biagini E, Barontini F, Tognotti L (2006) Devolatilization of biomass fuels and biomass components studied by TG/FTIR technique. Ind Eng Chem Res 45:4486–4493

Bradbury AG, Sakai Y, Shafizadeh F (1979) A kinetic model for pyrolysis of cellulose. J Appl Polym Sci 23:3271–3280

Bridgeman TG, Jones JM, Shield I, Williams PT (2008) Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel 87:844–856

Chen W (2012) Fixed bed counter current low temperature gasification of mesquite and juniper biomass using air-steam as oxidizer. PhD Dissertation, Texas A&M University

Chen WH, Kuo PC (2010a) A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry. Energy 35(6):2580–2586

Chen WH, Kuo PC (2010b) Torrefaction and co-torrefaction of hemicellulose, cellulose and lignin as well as torrefaction of the some basic constituents in biomass. Energy 36(2):803–811

Chen WH, Hsu HC, Lu KM, Lee WJ, Lin TC (2011) Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass. Energy 36(5):3012–3021

Cozzani V, Lucchesi A, Stoppato G, Maschio G (1997) A new method to determine the composition of biomass by thermogravimetric analysis. Can J Chem Eng 75:127–133

Demirbaş A (2005) Estimating of structural composition of wood and non-wood biomass samples. Energy Sources 27(8):761–767

Di Blasi C (2008) Modeling chemical and physical processes of wood and biomass pyrolysis. Prog Energy Combust Sci 34:47–90

EIA (2013) EIA total energy data. http://www.eia.gov/totalenergy/data/annual/showtext.cfm?t=ptb0804a

Eseltine D (2011) Effect of using inert and non-inert gases on the thermal degradation and fuel properties of biomass in the torrefaction and pyrolysis region, MS thesis, Texas A&M University

Eseltine D, Thanapal SS, Annamalai K, Ranjan D (2013) Torrefaction of woody biomass (juniper and mesquite) using inert and non-inert gases. Fuel 113:379–388

Faix O, Jakab E, Till F, Székely T (1988) Study on low mass thermal degradation products of milled wood lignins by thermogravimetry-mass-spectrometry. Wood Sci Technol 22:323–334

Ferdous D, Dalai AK, Bej SK, Thring RW (2002) Pyrolysis of lignins: experimental and kinetics studies. Energy Fuels 16:1405–1412

Hall WS (1905) A Textbook of physiology, 2nd edn. Lea, New York

Heller MC, Keoleian GA, Volk TA (2003) Life cycle assessment of a willow bioenergy cropping system. Biomass Bioenergy 25:147–165

Hu S, Jess A, Xu M (2007) Kinetic study of chinese biomass slow pyrolysis: comparison of different kinetic models. Fuel 86:2778–2788

Jacobson K, Maheria KC, Kumar Dalai A (2013) Bio-oil valorization: a review. Renew Sustain Energy Rev 23:91–106

Lawrence B, Annamalai K, Sweeten JM, Heflin K (2009) Cofiring coal and dairy biomass in a 29 kWt furnace. Appl Energy 86(11):2359–2372

Liu Q, Wang S, Zheng Y, Luo Z, Cen K (2008) Mechanism study of wood lignin pyrolysis by using TG–FTIR analysis. J Anal Appl Pyrol 82:170–177

Manya JJ, Velo E, Puigjaner L (2003) Kinetics of biomass pyrolysis: a reformulated three-parallel-reactions model. Ind Eng Chem Res 42:434–441

McClave SA, Lowen CC, Kleber MJ, McConnell JW, Jung LY, Goldsmith LJ (2003) Clinical use of the respiratory quotient obtained from indirect calorimetry. J Parenter Enteral Nutr 27:21–26

McKendry P (2002) Energy production from biomass (part 1): overview of biomass. Bioresour Technol 83:37–46

Mészáros E, Várhegyi G, Jakab E, Marosvölgyi B (2004) Thermogravimetric and reaction kinetic analysis of biomass samples from an energy plantation. Energy Fuels 18:497–507

Morinaka T, Wozniewicz M, Jeszka J, Bajerska J, Limtrakul PN, Makonkawkeyoon L, Hirota N, Kumagai S, Sone Y (2012) Comparison of seasonal variation in the fasting respiratory quotient of young Japanese, Polish and Thai women in relation to seasonal change in their percent body fat. J Physiol Anthropol 31:10

Orfao JJM, Antunes FJA, Figueiredo JL (1999) Pyrolysis kinetics of lignocellulosic materials—three independent reactions model. Fuel 78:349–358

Ozawa T (1965) A new method of analyzing thermogravimetric data. Bull Chem Soc Japan 38:1881–1886

Peng Y, Wu S (2010) The structural and thermal characteristics of wheat straw hemicellulose. J Anal Appl Pyrol 88:134–139

Prins MJ, Kryzysztof JP, Janssen FJJG (2006a) More efficient gasification via torrefaction. Energy 31(15):3458–3470

Prins MJ, Kryzysztof JP, Janssen FJJG (2006b) Torrefaction of wood: part 2. Analysis of products. Energy 77(1):35–40

Prins MJ, Ptasinski KJ, Janssen FJ (2006c) Torrefaction of wood: part 1. Weight loss kinetics. J Anal Appl Pyrol 77:28–34

Raveendran K, Ganesh A, Khilar KC (1996) Pyrolysis characteristics of biomass and biomass components. Fuel 75:987–998

Repellin V, Govin A, Rolland M, Guyonnet R (2010) Modelling anhydrous weight loss of wood chips during torrefaction in a pilot kiln. Biomass Bioenergy 34:602–609

Richardson HB (1929) The respiratory quotient. Physiol Rev 9:61–125

Rizzo MR, Mari D, Barbieri M, Ragno E, Grella R, Provenzano R, Villa I, Esposito K, Giugliano D, Paolisso G (2005) Resting metabolic rate and respiratory quotient in human longevity. J Clin Endocrinol Metab 90:409–413

Rousset P, Macedo L, Commandré JM, Moreira A (2012) Biomass torrefaction under different oxygen concentrations and its effect on the composition of the solid by-product. J Anal Appl Pyrol 96:86–91

Sonobe T, Worasuwannarak N (2008) Kinetic analyses of biomass pyrolysis using the distributed activation energy model. Fuel 87:414–421

TAMU (2013) TAMU fuel data bank. http://cabel.tamu.edu/TAMU%20FDB.htm

Thanapal SS (2014) Effect of cofiring torrefied woody biomass with coal in a 30 kWt downfired burner. PhD dissertation, Texas A&M University

Thanapal SS, Chen W, Annamalai K, Carlin N, Ansley RJ, Ranjan D (2014) Carbon dioxide torrefaction of woody biomass. Energy Fuels 28:1147–1157

Tillman D, Duong D, Harding N (2012) Solid fuel blending; principles, practices, and problems, 1st edn. Heinemann, Butterworth

Vamvuka D, Kakaras E, Kastanaki E, Grammelis P (2003) Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite. Fuel 82:1949–1960

Van de Weerdhof MW (2010) Modeling the pyrolysis process of biomass particles. Masters Thesis, Eindhoven University of Technology

Varhegyi G, Antal MJ Jr, Szekely T, Szabo P (1989) Kinetics of the thermal decomposition of cellulose, hemicellulose, and sugarcane bagasse. Energy Fuels 3:329–335

Varhegyi G, Antal MJ Jr, Jakab E, Szabó P (1997) Kinetic modeling of biomass pyrolysis. J Anal Appl Pyrol 42:73–87

Wang C, Peng J, Li H, Bi XT, Legros R, Lim CJ, Sokhansanj S (2012a) Oxidative torrefaction of biomass residues and densification of torrefied sawdust to pellets. Bioresour Technol 127:318–325

Wang XY, Wan XJ, Chen MQ, Wang J (2012b) Kinetic model of biomass pyrolysis based on three-component independent parallel first-order reactions. Chin J Process Eng 12:1020–1024

Wu YM, Zhao ZL, Li HB, Fang HE (2009) Low temperature pyrolysis characteristics of major components of biomass. J Fuel Chem Technol 37(4):427–432

Yan W, Hastings JT, Acharjee TC, Coronella CJ, Vasquez VR (2010) Mass and energy balances of wet torrefaction of lignocellulosic biomass. Energy Fuels 24:4738–4742

Yang H, Yan R, Chen H, Lee DH, Zheng C (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86:1781–1788

Yoon HC, Pozivil P, Steinfeld A (2011) Thermogravimetric pyrolysis and gasification of lignocellulosic biomass and kinetic summative law for parallel reactions with cellulose, xylan, and lignin. Energy Fuels 26:357–364